Exact results for state-to-state transition probabilities in the multistate Landau-Zener model by non-stationary perturbation theory

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Abstract

Multistate generalizations of Landau-Zener model are studied by summing entire series of perturbation theory. A new technique for analysis of the series is developed. Analytical expressions for probabilities of survival at the diabatic potential curves with extreme slope are proved. Degenerate situations are considered when there are several potential curves with extreme slope. New expressions for some state-to-state transition probabilities are derived in degenerate cases.

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I. INTRODUCTION

The famous Landau-Zener two-state model, introduced and solved in 1932 by Landau [1], Zener [2], Majorana [3] and Stückelberg [4] finds many applications in atomic physics and beyond. This is due to its virtue of describing generic case of non-adiabatic transitions in quantum mechanics. The main feature of the exactly solvable quantum model is the linear dependence of the matrix Hamiltonian on time. The model allows the derivation of exact expression for the state-to-state transition probability.

The natural generalization of the two-state model is the model with arbitrary (but still finite) number of states, N. The linear dependence of matrix Hamiltonian on time is retained $\mathbf{H}(t) = \mathbf{A} + \mathbf{B}t$, where \mathbf{A} and \mathbf{B} are time-independent $N \times N$ matrices. Hereafter we show by bold type the operators and vectors in N-dimensional linear space. The lower case characters are used to denote vectors in this space while the capital characters denote matrix operators.

Without loss of generality one might assume that the basis is chosen in such a way that the Hermitian matrix \mathbf{B} is diagonal, $B_{jk} = \beta_j \delta_{jk}$, where the parameters β have the meaning of slopes of linear diabatic potential curves. The so chosen basis is known as the *diabatic basis*. The non-diagonal elements of matrix \mathbf{A} have the meaning of couplings between the diabatic states, $A_{jk} = V_{jk}$. The diagonal matrix elements of \mathbf{A} play a different role. It is convenient to introduce for them a special notation, $\varepsilon_j = A_{jj}$ (these notations are the same as in our preceding studies [11, 13, 14]). The diagonal matrix elements of the Hamiltonian $\mathbf{H}(t)$ are referred to as *diabatic potential curves*. In the case of the multistate Landau-Zener model, they are linear in time, $E_j^{\text{dia}}(t) = \beta_j t + \varepsilon_j$.

The problem is to solve the non-stationary Schrödinger equation

$$i\frac{d\mathbf{c}}{dt} = \mathbf{H}(t) \mathbf{c} , \qquad (1.1)$$

and to find S-matrix. Generally speaking the full exact solution of (1.1) is not available. The known exact solutions [5, 6, 7, 8] refer to special choices of the model parameters β_j , ε_j , V_{jk} , such that the quantum interference oscillations do not appear in the transition probabilities. Furthermore, even in the case of the most general form of matrix Hamiltonian one can exactly find two elements of S-matrix which correspond to survival on the diabatic potential curves with extremal (maximum or minimum) slopes. The simple formula for such elements was originally guessed by S. Brundobler and V. Elzer [9] based on numerical calculations.

The proof of Brundobler-Elzer (BE) formula was carried out recently by several different ways. A. V. Shytov obtained this formula via treatment within the contour integration approach [10]. M. V. Volkov and V N Ostrovsky carried out the proof using non-stationary perturbation theory [11]. However there are some oversights in this proof, as B. E. Dobrescu and N. A. Sinitsyn indicated in the comment to this paper [12]. The comment contains a new proof of BE formula partly based on developments by Volkov and Ostrovsky; at the crucial step it essentially uses results for the bow-tie model [6] exactly solved by Ostrovsky and Nakamura.

The objective of the present study is to provide a proof of the BE formula which is devoid of deficiency of the previously suggested proof being fully based on analysis of non-stationary perturbation theory and summation of an entire perturbative expansion. Compared to the case of a Hamiltonian $\mathbf{H}_{\text{bound}}(t)$ with all the matrix element bounded $[(H_{\text{bound}})_{jk}(t) < a$ for all times t] the case of the multistate Landau-Zener Hamiltonian provides important specifics. The emerging integrals typically contain highly oscillating exponential factors that ensure integral convergence. For some choice of parameters in the integrand the oscillations vanish which means that the integral is a singular function of parameters. These singularities are to be treated in the analysis with proper care; albeit namely the presence of singularities allows a closed-form evaluation for each term of the entire series with subsequent analytical summation.

In the main Section III we develop a new approach to treat the singularities. The preliminary Section II introduces notations and contains a general description of the perturbative series. In distinction to the scheme suggested by Dobrescu and Sinitsyn [12], our proof (Section III) does not use results of any exactly solvable model. We believe that such a complete treatment of the perturbative expansion with analytical summation of series is of general interest.

Another goal of our study is to consider some degenerate cases (Section IV). Here more state-to-state probabilities can be evaluated, up to the fully degenerate multistate model where an entire matrix of state-to-state transition probabilities is found (Section IV D).

II. NON-STATIONARY PERTURBATION THEORY

The well-known formula for transition probability for two-state linear model was derived by Zener by reducing the Schrödinger equation to an equation for a hyperbolic cylinder function [2]. Majorana [3] used contour integration method in a complex plane to solve the same problem. Much later Kayanuma suggested an alternative approach [15, 16] where the non-stationary perturbation theory is used. As discussed in the Introduction, we in the present paper provide a generalization of this method to the multistate case.

The non-stationary Schrödinger equation (1.1) might be written as the set of N coupled first-order differential equations:

$$i\frac{dc_j}{dt} = \varepsilon_j c_j + \beta_j t c_j + \sum_{k \neq j} V_{jk} c_k , \qquad j, \ k = 1, 2, \dots N .$$
 (2.1)

After phase transformation which eliminates the diagonal elements on the right-hand side of equations (2.1) it takes the form

$$i\frac{da_j}{dt} = \sum_{k \neq j} V_{jk} \exp\left[i\left((\varepsilon_j - \varepsilon_k)t + \frac{1}{2}(\beta_j - \beta_k)t^2\right)\right] a_k , \qquad j, \ k = 1, 2, \dots N . \tag{2.2}$$

The integral form of this equation

$$a_j(t) = a_j(-\infty) - i \int_{-\infty}^t dt_0 \sum_{k \neq j} V_{jk} \exp\left[i(\varepsilon_j - \varepsilon_k)t_0 + \frac{i}{2}(\beta_j - \beta_k)t_0^2\right] a_k(t_0)$$
 (2.3)

is convenient for an iterative solution. The successive approximations, $a_j^{(n)}(t_n)$, are found by iterations:

$$a_j^{(n+1)}(t_{n+1}) = a_j^{(0)}(-\infty) - i \int_{-\infty}^{t_{n+1}} dt_n \sum_{k \neq j} V_{jk} \exp\left[i(\varepsilon_j - \varepsilon_k)t_n + i\frac{1}{2}(\beta_j - \beta_k)t_n^2\right] a_k^{(n)}(t_n)(2.4)$$

We use label 1 for the initially populated state, so that initial populations $a_j(-\infty)$ are

$$a_j(-\infty) = \delta_{j1} \ . \tag{2.5}$$

Then transition probability to j-th state is

$$P_{1j} = \left| \lim_{n \to \infty} a_j^{(n)}(+\infty) \right|^2 . \tag{2.6}$$

In the next formula we introduce a vector-function of time $\mathbf{f}(t) = \{f_1(t), f_2(t) \dots f_N(t)\},\$ which is a vector in N-dimensional linear space. The operator \mathbf{T} is $N \times N$ matrix; it

transforms the vector-function $\mathbf{f}(t)$ into another vector-function with components:

$$\left[\hat{\mathbf{T}}\mathbf{f}\right]_{j}(t_{n+1}) \equiv (-i)\sum_{\substack{k=1\\k\neq j}}^{N} V_{jk} \int_{-\infty}^{t_{n+1}} dt_{n} \exp\left[i(\varepsilon_{j} - \varepsilon_{k})t_{n} + \frac{i}{2}(\beta_{j} - \beta_{k})t_{n}^{2}\right] f_{k}(t_{n}) . (2.7)$$

With respect to the time variable the operator T is an integral operator. Our equations (2.4) can be written as

$$\mathbf{a}^{(n+1)} = \mathbf{a}^{(0)} + \hat{\mathbf{T}}\mathbf{a}^{(n)} , \qquad (2.8)$$

where dependence on time is implicit. The zero iteration $\mathbf{a}^{(0)}$ is defined by the initial conditions (2.5): $a_j^{(0)} = \delta_{j1}$.

We further introduce the vector \mathbf{d}^1 in N-dimensional linear space by a formula describing its components d_i^1 :

$$d_j^{(1)}(t) \equiv -iV_{j1} \int_{-\infty}^t dt_1 \exp\left[i(\varepsilon_j - \varepsilon_1)t_1 + \frac{i}{2}(\beta_j - \beta_1)t_1^2\right], \quad j \neq 1.$$
 (2.9)

The j=1 component $d_1^{(1)}$ is assumed to be zero by definition. Similarly, the vector $\mathbf{d}_j^{(m)}$ $(m \geq 2)$ is given as

$$d_{j}^{(m)}(t) \equiv (-i)^{m} \sum_{k_{m-1}\neq j}^{N} V_{jk_{m-1}} \sum_{k_{m-2}\neq k_{m-1}}^{N} V_{k_{m-1}k_{m-2}} \dots \sum_{k_{2}\neq k_{3}}^{N} V_{k_{3}k_{2}} \sum_{\substack{k_{1}\neq k_{2}\\k_{1}\neq 1}}^{N} V_{k_{2}k_{1}} V_{k_{1}1}$$

$$\times \int_{-\infty}^{t} dt_{m} \int_{-\infty}^{t_{m}} dt_{m-1} \dots \int_{-\infty}^{t_{2}} dt_{1}$$

$$\times \exp \left[i(\varepsilon_{j} - \varepsilon_{k_{m-1}})t_{m} + i \sum_{i=2}^{m-1} (\varepsilon_{k_{i}} - \varepsilon_{k_{i-1}})t_{i} + i(\varepsilon_{k_{1}} - \varepsilon_{1})t_{1} \right]$$

$$\times \exp \left[\frac{i}{2} (\beta_{j} - \beta_{k_{m-1}})t_{m}^{2} + \frac{i}{2} \sum_{i=2}^{m-1} (\beta_{k_{i}} - \beta_{k_{i-1}})t_{i}^{2} + \frac{i}{2} (\beta_{k_{1}} - \beta_{1})t_{1}^{2} \right] . \quad (2.10)$$

If the couplings are small, then the order of magnitude estimates are $T \sim V$, $\mathbf{d}^{(m)} \sim V^m$. Note the important relations between operator $\hat{\mathbf{T}}$ and vectors $\mathbf{d}^{(m)}$:

$$\hat{\mathbf{T}}\mathbf{d}^{(m)} = \mathbf{d}^{(m+1)}, \qquad m = 1, 2, \dots,$$

$$\hat{\mathbf{T}}\mathbf{a}^{(0)} = \mathbf{d}^{(1)}. \tag{2.11}$$

Using these relations and equation (2.8) we express the n-th iteration to \mathbf{a} as

$$\mathbf{a}^{(n)} = \mathbf{a}^{(0)} + \sum_{m=1}^{n} \mathbf{d}^{(m)} . \tag{2.12}$$

Formula (2.12) is the basis for all subsequent analysis. In order to find some transition amplitude one should evaluate the corrections (2.10) to all orders m in the limit $t \to +\infty$, then sum up all corrections using equation (2.12) with $n \to +\infty$. The sought for probability is given by formula (2.6).

III. PROOF OF THE BRUNDOBLER-ELZER FORMULA

A. Preliminary transformations: change of variables

Consider the case when the initially populated non-degenerated diabatic potential curve has ES, i.e. its slope is the largest $(\beta_1 = \max_j \beta_j)$ or the smallest $(\beta_1 = \min_j \beta_j)$ of all slopes. Here we set out to find the survival probability on such a potential curve. The general vector formula (2.12) for the first component reads

$$a_1^{(n)} = a_1^{(0)} + \sum_{m=1}^n d_1^{(m)} = 1 + \sum_{m=1}^n d_1^{(m)}$$
 (3.1)

The arbitrary term in the sum is given by (2.10) and (2.9). In the limit $t \to \infty$ and after reducing the brackets we obtain:

$$d_{1}^{(m)}(\infty) = (-i)^{m} \sum_{k_{m-1}\neq 1}^{N} V_{1k_{m-1}} \sum_{k_{m-2}\neq k_{m-1}}^{N} V_{k_{m-1}k_{m-2}} \dots \sum_{k_{2}\neq k_{3}}^{N} V_{k_{3}k_{2}} \sum_{\substack{k_{1}\neq k_{2}\\k_{1}\neq 1}}^{N} V_{k_{2}k_{1}} V_{k_{1}1}$$

$$\times \int_{-\infty}^{\infty} dt_{m} \int_{-\infty}^{t_{m}} dt_{m-1} \dots \int_{-\infty}^{t_{2}} dt_{1}$$

$$\times \exp \left[i\varepsilon_{1}(t_{m}-t_{1}) + i \sum_{i=1}^{m-1} \varepsilon_{k_{i}}(t_{i}-t_{i+1}) \right]$$

$$\times \exp \left[\frac{i}{2}\beta_{1}(t_{m}^{2}-t_{1}^{2}) + \frac{i}{2} \sum_{i=1}^{m-1} \beta_{k_{i}}(t_{i}^{2}-t_{i+1}^{2}) \right]. \tag{3.2}$$

Let us now introduce new integration variables $\{x_1, \ldots, x_m\}$ such that:

$$x_m = t_m, x_m \in (-\infty, \infty);$$

 $x_j = t_{j+1} - t_j, x_j \in (0, \infty), j = 1, 2 \dots, m-1.$ (3.3)

The important advantage of this transformation is that the ranges of variation of the new variables are simple and unambiguous, cf. discussion in Refs. [12, 13]. The Jacobian of the

transformation is equal to $(-1)^{m-1}$, the inverse transformation is given by

$$t_j = x_m - \sum_{k=j}^{m-1} x_k , \qquad j = 1, 2, \dots, m-1 ;$$

$$t_m = x_m . \tag{3.4}$$

In order to express the integrand in (3.2) in new variables the following formulas are useful:

$$t_{m} - t_{1} = \sum_{k=1}^{m-1} x_{k};$$

$$t_{m}^{2} - t_{1}^{2} = 2x_{m} \sum_{k=1}^{m-1} x_{k} - \left(\sum_{k=1}^{m-1} x_{k}\right)^{2};$$

$$t_{i}^{2} - t_{i+1}^{2} = 2x_{m}(-x_{i}) + x_{i} \left(x_{i} + 2\sum_{k=i+1}^{m-1} x_{k}\right) \qquad i = 1, \dots, m-2;$$

$$t_{m-1}^{2} - t_{m}^{2} = -2x_{m}x_{m-1} + x_{m-1}^{2}.$$

$$(3.5)$$

In new variables the integral is cast as

$$d_{1}^{m} = (-i)^{m} \sum_{k_{m-1}\neq 1}^{N} V_{1k_{m-1}} \sum_{k_{m-2}\neq k_{m-1}}^{N} V_{k_{m-1}k_{m-2}} \dots \sum_{k_{2}\neq k_{3}}^{N} V_{k_{3}k_{2}} \sum_{\substack{k_{1}\neq k_{2}\\k_{1}\neq 1}}^{N} V_{k_{2}k_{1}} V_{k_{1}1}$$

$$\times \int_{-\infty}^{\infty} dx_{m} \int_{0}^{\infty} dx_{m-1} \dots \int_{0}^{\infty} dx_{1} \exp\left[i\varepsilon_{1} \sum_{n=1}^{m-1} x_{n} - i \sum_{n=1}^{m-1} \varepsilon_{k_{n}} x_{n}\right]$$

$$\times \exp\left[\frac{i}{2}\beta_{1} \left(2x_{m} \sum_{n=1}^{m-1} x_{n} - \left(\sum_{n=1}^{m-1} x_{n}\right)^{2}\right)\right]$$

$$\times \exp\left[\frac{i}{2} \sum_{n=1}^{m-2} \beta_{k_{n}} \left(2x_{m}(-x_{n}) + x_{n} \left(x_{n} + 2 \sum_{j=n+1}^{m-1} x_{j}\right)\right)\right]$$

$$\times \exp\left[\left(-2x_{m} x_{m-1} + x_{m-1}^{2}\right) \beta_{k_{m-1}}\right]. \tag{3.6}$$

The integration over dx_m in infinite limits gives a δ -function. After reducing brackets in the exponents one obtains

$$d_{1}^{m} = (-i)^{m} \sum_{k_{m-1}\neq 1}^{N} V_{1k_{m-1}} \sum_{k_{m-2}\neq k_{m-1}}^{N} V_{k_{m-1}k_{m-2}} \dots \sum_{k_{2}\neq k_{3}}^{N} V_{k_{3}k_{2}} \sum_{\substack{k_{1}\neq k_{2}\\k_{1}\neq 1}}^{N} V_{k_{2}k_{1}} V_{k_{1}1}$$

$$\times \int_{0}^{\infty} dx_{m-1} \dots \int_{0}^{\infty} dx_{1} \exp \left[i \sum_{n=1}^{m-1} (\varepsilon_{1} - \varepsilon_{k_{n}}) x_{n} \right]$$

$$\times \exp \left[-\frac{i}{2} \sum_{n=1}^{m-1} (\beta_{1} - \beta_{k_{n}}) x_{n}^{2} - i \sum_{n=1}^{m-2} (\beta_{1} - \beta_{k_{n}}) x_{n} \sum_{j=n+1}^{m-1} x_{j} \right]$$

$$\times 2\pi \delta \left[\sum_{n=1}^{m-1} (\beta_{1} - \beta_{k_{n}}) x_{n} \right] . \tag{3.7}$$

The subsequent analysis of the multiple integral in (3.7) essentially depends on how much of the indices k_n are equal unity. At first we will consider the case when all indices are different from unity. Subsequently the integral with an arbitrary set of indices will be evaluated. Note that in this subsection we do not use the condition that the slope β_1 is extremal. However in the next subsection this assumption becomes essential.

B. The case with $k_n \neq 1$ for all n

We carry out a new change of integration variables in such a way that the argument of the δ -function in (3.7) depends on a single new variable:

$$y_i = \sum_{n=1}^{i} (\beta_1 - \beta_{k_n}) x_n , \qquad i = 1, 2, \dots, m-1 .$$
 (3.8)

The integration limits in the new variables has a simple form due to the fact that β_1 has extreme value compared with all another slopes. For the sake of definiteness we assume that $\beta_1 = \max_j \beta_j$, then

$$y_{m-1} \in (0, \infty)$$
,
 $y_i \in (0, y_{i+1}), \qquad i = 1, 2, \dots, m-2$. (3.9)

The modulus of the Jacobian for this transformation is

$$|J| = \prod_{n=1}^{m-1} \frac{1}{|\beta_1 - \beta_{k_n}|} . \tag{3.10}$$

Let us denote the multiple integral in (3.7) as I. Then in new variables we have

$$I = 2\pi |J| \int_0^\infty dy_{m-1} \, \delta(y_{m-1}) \int_0^{y_{m-1}} dy_{m-2} \cdots \int_0^{y_2} dy_1 \, f(y_1, y_2, \dots, y_{m-2}, y_{m-1}) \,, \quad (3.11)$$

where $f(y_1, y_2, ..., y_{m-2}, y_{m-1})$ is a regular (smooth) function of all its arguments. One can see that the integration over dy_{m-1} with $\delta(y_{m-1})$ in the integrand implies that $y_{m-1} \to 0$. This contracts the integration range over all other variables to zero. Thus, the entire integral I is zero.

C. The case with arbitrary set of indices

Let us assume that (p-1) of indices in (3.7) are equal to one, where $p \leq m$. Taking into account the obvious restrictions $(k_1 \neq 1 \text{ and } k_{m-1} \neq 1 \text{ and } k_{i+1} \neq k_i)$, one obtains a limitation for p: $p \leq \frac{1}{2}m$ for even m and $p \leq \frac{1}{2}(m-1)$ for odd m. In order to evaluate I in this case we need new notations. Let us introduce a string of integers $\mathcal{S} = \{s_1, s_2, \ldots, s_{p-1}\}$ that includes all the labels s_j such that $k_{s_j} = 1$. It is an ordered set, so that $s_{i+1} > s_i$. The complementary string $\mathcal{C} = \{c_1, c_2, \ldots, c_{m-p}\}$ includes all labels c_j such that $k_{c_j} \neq 1$ and also is ordered: $c_{i+1} > c_i$. The multiple integral in (3.7) is

$$I = \int_{0}^{\infty} dx_{c_{1}} \int_{0}^{\infty} dx_{c_{2}} \cdots \int_{0}^{\infty} dx_{c_{m-p}} \exp \left[i \sum_{n \in \mathcal{C}} (\varepsilon_{1} - \varepsilon_{k_{n}}) x_{n} \right]$$

$$\times \exp \left[-\frac{i}{2} \sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n}^{2} - i \sum_{\substack{n \in \mathcal{C} \\ n \neq m-1}} (\beta_{1} - \beta_{k_{n}}) x_{n} \sum_{\substack{j > n \\ j \in \mathcal{C}}} x_{j} \right] 2\pi \delta \left[\sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n} \right]$$

$$\times \int_{0}^{\infty} dx_{s_{1}} \int_{0}^{\infty} dx_{s_{2}} \cdots \int_{0}^{\infty} dx_{s_{p-1}} \exp \left[-i \sum_{\substack{n \in \mathcal{C} \\ n \neq m-1}} \sum_{\substack{j > n \\ j \in \mathcal{S}}} (\beta_{1} - \beta_{k_{n}}) x_{n} x_{j} \right]. \tag{3.12}$$

The integration variables belonging to S string enter exponent linearly (while other variables provide quadratic terms as well). This allows us to carry out integration in semiinfinite interval using the formula:

$$\int_0^\infty e^{ikx}dk = i\mathcal{P}\frac{1}{x} + \pi\delta(x) . \tag{3.13}$$

Here $\mathcal{P}^{\frac{1}{x}}$ indicates integration in the principal value sense. After this (3.12) reduces to

$$I = \int_{0}^{\infty} dx_{c_{1}} \int_{0}^{\infty} dx_{c_{2}} \cdots \int_{0}^{\infty} dx_{c_{m-p}} \exp \left[i \sum_{n \in \mathcal{C}} (\varepsilon_{1} - \varepsilon_{k_{n}}) x_{n} \right]$$

$$\times \exp \left[-\frac{i}{2} \sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n}^{2} - i \sum_{\substack{n \in \mathcal{C} \\ n \neq m-1}} (\beta_{1} - \beta_{k_{n}}) x_{n} \sum_{\substack{j > n \\ j \in \mathcal{C}}} x_{j} \right] 2\pi \delta \left[\sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n} \right]$$

$$\times \prod_{j \in \mathcal{S}} \left[\pi \delta \left(-\sum_{\substack{n \in \mathcal{C} \\ n \neq m-1}} (\beta_{1} - \beta_{k_{n}}) x_{n} \right) + i \mathcal{P} \frac{1}{-\sum_{\substack{n \in \mathcal{C} \\ n \neq m-1}} (\beta_{1} - \beta_{k_{n}}) x_{n}} \right].$$

$$(3.14)$$

Now a change of variables (3.8) is conveniently modified to

$$y_{i} = \sum_{n=1}^{i} (\beta_{1} - \beta_{k_{c_{n}}}) x_{c_{n}}, \qquad i = 1, 2, \dots, m - p,$$

$$y_{m-p} \in (0, \infty),$$

$$y_{i} \in (0, y_{i+1}), \qquad i = 1, 2, \dots, m - p - 1.$$

$$(3.15)$$

The Jacobian modulus is

$$|J| = \prod_{n \in \mathcal{C}} \frac{1}{|\beta_1 - \beta_{k_n}|} \ . \tag{3.16}$$

Each of delta-functions in formula (3.14) depend only on single new variable y_i , so that this formula is cast as

$$I = 2\pi |J| \int_{0}^{\infty} dy_{m-p} \, \delta(y_{m-p}) \int_{0}^{y_{m-p}} dy_{m-p-1} \cdots \int_{0}^{y_{2}} dy_{1} \, f(y_{1}, y_{2}, \dots, y_{m-p})$$

$$\times \prod_{j=1}^{p-1} \left[\pi \delta(-y_{s_{j}-j}) + i \mathcal{P} \frac{1}{-y_{s_{j}-j}} \right], \qquad (3.17)$$

where $f(y_1, y_2, ..., y_{m-p})$ is a regular function of all its arguments. As in previous subsection, the integration over dy_{m-p} with δ -function contracts to one point, namely zero, the range of integration over all other variables; thus it could be said that the contribution from the \mathcal{P} -terms is zero because of identity

$$\int_0^y \mathcal{P}\frac{1}{x}f(x)\,dx \to 0 \tag{3.18}$$

for $y \to 0$ and f(x) non-singular at x = 0. Therefore the entire integral is different from zero only if integrand is singular function of all its variable. It could be only if the number of integrals in (3.17) equals the number of δ -functions in integrand. This reasoning give us the condition m - p = p - 1 + 1, i.e. m = 2p. This means that only even terms in the expansion (3.1) give non-zero contributions. The string \mathcal{S} consists of $(\frac{1}{2}m - 1)$ numbers. Taking into account the inequalities $k_{i+1} \neq k_i$, $k_1 \neq 1$, $k_{m-1} \neq 1$ we obtain the necessary condition for indices in (3.7):

$$k_{2j} = 1$$
 for $j = 1, 2, \dots, \frac{1}{2}m - 1$. (3.19)

In other words the following indices have the value 1:

$$k_2, k_4, k_6, \dots k_{m-4}, k_{m-2}$$
 (3.20)

D. Summation of non-zero contributions

For an arbitrary term in (3.1) we obtain

$$d_{1}^{2p-1} = 0 ,$$

$$d_{1}^{2p} = (-1)^{p} 2\pi^{p} \sum_{k_{2p-1} \neq 1}^{N} V_{1k_{2p-1}} V_{k_{2p-1}1} \dots \sum_{k_{3} \neq 1}^{N} V_{1k_{3}} V_{k_{3}1} \sum_{k_{1} \neq 1}^{N} V_{1k_{1}} V_{k_{1}1}$$

$$\times \prod_{j=1}^{p} \frac{1}{|\beta_{1} - \beta_{k_{2j-1}}|} \int_{0}^{\infty} dy_{p} \int_{0}^{y_{p}} dy_{p-1} \dots \int_{0}^{y_{2}} dy_{1}$$

$$\times f(y_{1}, y_{2}, \dots, y_{p}) \prod_{j=1}^{p} \delta(y_{j}) , \qquad p = 1, 2, \dots$$

$$(3.21)$$

The product of δ -functions in the last expression makes the integrand to be symmetrical function with respect to arbitrary permutations of the integration variables $\{y_1, y_2, \dots, y_p\}$. Besides this, the integrand is an even function of any of its argument that allows us to

extend the limits of integration:

$$d_{1}^{2p} = (-1)^{p} 2\pi^{p} \frac{1}{2p!} \sum_{k_{2p-1}\neq 1}^{N} V_{1k_{2p-1}} V_{k_{2p-1}1} \dots \sum_{k_{3}\neq 1}^{N} V_{1k_{3}} V_{k_{3}1} \sum_{k_{1}\neq 1}^{N} V_{1k_{1}} V_{k_{1}1}$$

$$\times \prod_{j=1}^{p} \frac{1}{|\beta_{1} - \beta_{k_{2j-1}}|} \int_{-\infty}^{\infty} dy_{1} \int_{-\infty}^{\infty} dy_{2} \dots \int_{-\infty}^{\infty} dy_{p} f(y_{1}, y_{2}, \dots, y_{p}) \prod_{i=1}^{p} \delta(y_{i})$$

$$= \frac{(-\pi)^{p}}{p!} \sum_{k_{2p-1}\neq 1}^{N} V_{1k_{2p-1}} V_{k_{2p-1}1} \dots \sum_{k_{1}\neq 1}^{N} V_{1k_{1}} V_{k_{1}1} \prod_{j=1}^{p} \frac{1}{|\beta_{1} - \beta_{k_{2j-1}}|}$$

$$= \frac{1}{p!} \left(\sum_{k\neq 1}^{N} \frac{-\pi V_{1k} V_{k_{1}}}{|\beta_{1} - \beta_{k}|} \right)^{p} . \tag{3.22}$$

Here we used the property f(0, 0, ..., 0) = 1.

For the survival amplitude in the limit $n \to \infty$ we have the exact expression:

$$a_1^{(\infty)} = 1 + \sum_{p=1}^{\infty} \frac{1}{p!} \left(\sum_{k \neq 1}^{N} \frac{-\pi V_{1k} V_{k1}}{|\beta_1 - \beta_k|} \right)^p = \exp\left(-\pi \sum_{k \neq 1}^{N} \frac{V_{1k} V_{k1}}{|\beta_1 - \beta_k|} \right). \tag{3.23}$$

Finally, for the survival probability we obtain BE formula:

$$P_{11} = |a_1(\infty)|^2 = \exp\left(-2\pi \sum_{k \neq 1}^N \frac{V_{1k}V_{k1}}{|\beta_1 - \beta_k|}\right).$$
 (3.24)

IV. EXTENSION OF THE APPROACH TO DIFFERENT DEGENERATE CASES

In this section we assume the presence of a special property of a Hamiltonian compared to general treatment of previous section. Namely, we presume degeneracy of the potential curves. As above we consider the situation when the initially populated state 1 has the largest $(\beta_1 = \max_j \beta_j)$ or the smallest $(\beta_1 = \min_j \beta_j)$ of all slopes, except slopes for the states 1, 2, ..., n $(j \neq 1, 2, ..., n)$. In other words, we presume degeneracy of extreme slopes, $\beta_1 = \beta_2 = \cdots = \beta_n$, or, in yet other words, there are n parallel curves with extreme slope. It is natural also to presume that the parallel curves are not coupled, i.e. $V_{ij} = 0$ for (i, j = 1, 2, ..., n).

The particular case when two bands of parallel potential curves received some attention in the literature [17, 18, 19, 20].

Subsequently we consider yet more special situation that the extreme slope curves are not only parallel, but fully degenerate, i.e. $\varepsilon_1 = \varepsilon_2 = \cdots = \varepsilon_n$.

A. The case of parallel diabatic potential curves with extremal slope

In this subsection we consider the case of n diabatic potential curves with the same extreme slope $\beta_i = \beta$ (i = 1, 2, ..., n) and $\beta = \max_{k>n} \{\beta_k\}$ or $\beta = \min_{k>n} \{\beta_k\}$. We also assume that $\varepsilon_i \neq \varepsilon_j$ and $V_{ij} = 0$, where $(i \neq j)$ and (i, j = 1, 2, ..., n). Such a model for n = 2 was considered in our previous work [14], where transition probability P_{12} for $(\varepsilon_2 > \varepsilon_1)$ was considered; now we concentrate on the survival probability. We will prove the formula for survival probability on the diabatic potential curve with extremal slope for n = 2. The proof for arbitrary n might be carry out similarly.

The survival amplitude a_1^m is again given by general formulas (3.1) and (3.7) but the subsequent analysis is a little more complicated. The string of integers \mathcal{S} is introduced as in the previous section. Besides this, we introduce a string of integers $\mathcal{R} = \{r_1, r_2, \ldots, r_g\}$, which includes all labels such that $k_{r_j} = 2$. It is also an ordered set: $r_{i+1} > r_i$. The complementary string $\mathcal{C} = \{c_1, c_2, \ldots, c_{m-p-g}\}$ includes all labels c_j such that $k_{c_j} \neq 1, 2$ and also is ordered: $c_{i+1} > c_i$. The dimensions of these strings have to satisfy the conditions:

$$p+g \le \frac{1}{2}m$$
 for even m ,
 $p+g \le \frac{1}{2}(m-1)$ for odd m , (4.1)

otherwise one or more of the couplings in (3.7) is zero. The multiple integral in (3.7) is in this case after integration, given through the formula (3.13):

$$I = \int_{0}^{\infty} dx_{c_{1}} \int_{0}^{\infty} dx_{c_{2}} \cdots \int_{0}^{\infty} dx_{c_{m-p-g}} \exp \left[i \sum_{n \in \mathcal{C}} (\varepsilon_{1} - \varepsilon_{k_{n}}) x_{n} \right]$$

$$\times \exp \left[-\frac{i}{2} \sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n}^{2} - i \sum_{j \in \mathcal{C}} x_{j} \sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n} \right] 2\pi \delta \left[\sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n} \right]$$

$$\times \prod_{j \in \mathcal{S}} \left[\pi \delta \left(-\sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n} \right) + i \mathcal{P} \frac{1}{-\sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n}} \right]$$

$$\times \prod_{j \in \mathcal{R}} \left[\pi \delta \left(-\sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n} + (\varepsilon_{1} - \varepsilon_{2}) \right) + i \mathcal{P} \frac{1}{-\sum_{n \in \mathcal{C}} (\beta_{1} - \beta_{k_{n}}) x_{n} + (\varepsilon_{1} - \varepsilon_{2})} \right] (4.2)$$

We realize the change of variables by formula (3.15) with the same Jacobian modulus

(3.16), but now the total amount of variables is (m-p-g). Note that every delta-function after such transformation depends on only one variable. In new variables the multiple integral is given by the expression:

$$I = 2\pi |J| \int_{0}^{\infty} dy_{m-p-g} \, \delta(y_{m-p-g}) \int_{0}^{y_{m-p-g}} dy_{m-p-g-1} \cdots \int_{0}^{y_{2}} dy_{1} \, f(y_{1}, y_{2}, \dots, y_{m-p-g})$$

$$\times \prod_{j=1}^{p-1} \left[\pi \delta(-y_{s_{j}-j-\alpha_{j}}) + i \mathcal{P} \frac{1}{-y_{s_{j}-j-\alpha_{j}}} \right]$$

$$\times \prod_{j=1}^{g} \left[\pi \delta(-y_{r_{j}-j-\beta_{j}} + \varepsilon_{1} - \varepsilon_{2}) + i \mathcal{P} \frac{1}{-y_{r_{j}-j-\beta_{j}} + \varepsilon_{1} - \varepsilon_{2}} \right]. \tag{4.3}$$

Here α_j is the number of the elements of the string \mathcal{R} which are less than s_j , β_j is the number of the elements of string \mathcal{S} which are less than r_j and $f(y_1, y_2, \ldots, y_{m-p-g})$ is a regular function of all its arguments. Note that all δ -functions in the integral depend on different variables.

The integration over dy_{m-p-g} with δ -function contracts to one point, namely zero, the range of integration over all other variables. Thus it could be said that the contribution from the \mathcal{P} -terms is zero because of identity (3.18). Furthermore the contribution from δ -functions in the second product in (4.3) is zero. The multiple integral is different from zero only if integrand is singular function of every integration variable. This only happens if the number of integrals in (4.3) equals the number of δ -functions in the integrand. This reasoning give us the condition m-p-g=p-1+1, i.e. m=2p+g. Note that if $g\neq 0$ this condition contradicts (4.1). Thus, this implies that g=0. Thereby we come to the same result: m=2p as in previous section. Besides this, we obtain the complementary condition $k_j\neq 2$ for $j=1,2,\ldots,m-1$.

The same calculations as in non-degenerate case give us the survival probability

$$P_{11} = |a_1(\infty)|^2 = \exp\left(-2\pi \sum_{k \neq 1,2}^N \frac{V_{1k}V_{k1}}{|\beta_1 - \beta_k|}\right). \tag{4.4}$$

For more general case of n-fold degeneracy (n < N) of extreme slope potential curves we similarly obtain

$$P_{jj} = |a_1(\infty)|^2 = \exp\left(-2\pi \sum_{k \neq 1, 2, \dots, n}^{N} \frac{V_{jk} V_{kj}}{|\beta_j - \beta_k|}\right) \qquad j = 1, 2 \dots, n.$$
 (4.5)

In case when a band of parallel potential curves is crossed by a single curve (n = N - 1) formula (4.5) reproduces an early result by Demkov and Osherov [5].

B. The case of merged diabatic potential curves with extremal slope

Consider the case when we have n diabatic potential curves with the same slope $\beta_i = \beta$ (i = 1, 2, ..., n) and $\beta = \max_{k>n} \{\beta_k\}$ or $\beta = \min_{k>n} \{\beta_k\}$. As distinct from previous subsection we assume that $\varepsilon_i = \varepsilon$ (i = 1, 2, ..., n). This means that the potential curves 1, 2, ..., n are merged. At first we will obtain expressions for survival probabilities for n = 2 and then will generalize them for arbitrary n.

In the case of two merged diabatic curves with extremal slope we assume the following conditions for couplings

$$V_{2i} = c_2 V_{1i} (4.6)$$

with some i-independent constant c_2 . Acting further as in non-degenerate case we obtain restrictions for the coefficients:

$$k_{2j} = 1, 2 \text{ for } j = 1, 2, \dots, \frac{1}{2}m - 1.$$
 (4.7)

For an arbitrary term in (3.1) we have after integrating:

$$d_{1}^{2p} = \frac{(-\pi)^{p}}{p!} \sum_{k_{2p-1} \neq 1,2}^{N} V_{1k_{2p-1}} \sum_{k_{2p-2}=1}^{2} V_{k_{2p-1}k_{2p-2}} \dots \sum_{k_{2}=1}^{2} V_{k_{3}k_{2}} \sum_{k_{1} \neq 1,2}^{N} V_{k_{2}k_{1}} V_{k_{1}1}$$

$$\times \prod_{j=1}^{p} \frac{1}{|\beta_{1} - \beta_{k_{2j-1}}|},$$

$$d_{1}^{2p-1} = 0.$$

$$(4.8)$$

Due to the property (4.7), summations over two terms, \sum_{1}^{2} , emerge here. Now we use condition (4.6) to get:

$$\sum_{k_{2j}=1}^{2} V_{k_{2j-1}k_{2j}} V_{k_{2j}k_{2j+1}} = V_{k_{2j-1}1} V_{1k_{2j+1}} + V_{k_{2j-1}2} V_{2k_{2j+1}} = \left(1 + c_2^2\right) V_{k_{2j-1}1} V_{1k_{2j+1}} \ . \tag{4.9}$$

Then formula (4.8) is rewritten as

$$d_1^{2p} = \frac{(-\pi)^p}{p!} (1 + c_2^2)^{p-1} \sum_{k_{2p-1} \neq 1, 2}^N V_{1k_{2p-1}} V_{k_{2p-1}} \dots \sum_{k_1 \neq 1, 2}^N V_{1k_1} V_{k_1 1} \left(\prod_{j=1}^p \frac{1}{|\beta_1 - \beta_{k_{2j-1}}|} \right)$$

$$= \frac{1}{1 + c_2^2} \left(\sum_{k \neq 1, 2}^N \frac{-(1 + c_2^2) \pi V_{1k} V_{k_1}}{|\beta_1 - \beta_k|} \right)^p \frac{1}{p!} ,$$

$$d_1^{2p+1} = 0 . \tag{4.10}$$

Obviously, d_1^{2p} are terms in the expansion of an exponent,

$$\frac{1}{(1+c_2^2)} \exp\left(\sum_{k\neq 1,2}^N \frac{-(1+c_2^2)\pi V_{1k} V_{k1}}{|\beta_1 - \beta_k|}\right) . \tag{4.11}$$

However, the first term in formula (3.1) is 1, that is different from the first term in the expansion of expression (4.11). This is easily taken into account. For survival probability we thus obtain

$$P_{11} = \frac{1}{(1+c_2^2)^2} \left[\exp\left(-(1+c_2^2) \sum_{k\neq 1,2}^N \frac{\pi V_{1k} V_{k1}}{|\beta_1 - \beta_k|}\right) + c_2^2 \right]^2.$$
 (4.12)

This result may be easily generalized to the case of n-fold degeneracy of the extreme slope potential curves with an arbitrary n. A simple generalization is possible under conditions

$$V_{ki} = c_k V_{1i}, \qquad j > n, \qquad k = 1, \dots, n,$$
 (4.13)

which state that the interaction of degenerate states 1, 2, ..., n with non-degenerate states (j > n) exhibit the same j-pattern, up to common factors c_k . Under these conditions for an arbitrary term in (3.1) we obtain

$$d_{1}^{2p} = (-1)^{p} C^{2p-2} \sum_{k_{2p-1}\neq 1, 2, \dots, n}^{N} V_{1k_{2p-1}} V_{k_{2p-1}1} \dots \sum_{k_{1}\neq 1, 2, \dots, n}^{N} V_{1k_{1}} V_{k_{1}1} \frac{\pi^{p}}{p!} \left(\prod_{j=1}^{p} \frac{1}{|\beta_{1} - \beta_{k_{2j-1}}|} \right)$$

$$= \frac{1}{C^{2}} \left(\sum_{k\neq 1, 2, \dots, n}^{N} \frac{-C^{2} \pi V_{1k} V_{k_{1}}}{|\beta_{1} - \beta_{k}|} \right)^{p} \frac{1}{p!} ,$$

$$d_{1}^{2p+1} = 0 ,$$

$$(4.14)$$

where $C^2 = \sum_{k=1}^n c_k^2$. For survival probability here we have

$$P_{11} = C^{-4} \left[\exp\left(-C^2 \sum_{k \neq 1, 2, \dots, n}^{N} \frac{\pi V_{1k} V_{k1}}{|\beta_1 - \beta_k|} \right) + C^2 - 1 \right]^2.$$
 (4.15)

We now turn to evaluation of transition probabilities between degenerated states 1, 2, ..., n. The expansion terms d_1^m (4.14) in fact do not depend on which of degenerate states is initially populated. Formally there is subscript 1 in d_1^m that indicates initial population, but it could be replaced by any j = 2, 3, ..., n without any other change in formulas, except for changing couplings $V_{1k_{2p-1}}$ to $V_{jk_{2p-1}}$.

However, there is difference in the first term of the perturbative expansion (3.1) that explicitly indicates the initial population. Taking this into account, it is easy to write down expression for probabilities of transitions within the submanifold of degenerate states:

$$P_{1j} = \frac{c_j^2}{C^4} \left[\exp\left(-C^2 \sum_{k \neq 1, 2, \dots, n}^{N} \frac{\pi V_{1k} V_{k1}}{|\beta_1 - \beta_k|}\right) - 1 \right]^2, \qquad j = 2, \dots, n.$$
 (4.16)

C. Alternative derivation via orthogonalization

Now we consider alternative scheme of derivation for the case when we have only two diabatic potential curves with the same slope $\beta_1 = \beta_2 = \beta$ and $\beta = \max_k \{\beta_k\}$ or $\beta = \min_k \{\beta_k\}$, and $\varepsilon_1 = \varepsilon_2$. As the conditions on couplings we again use formula (4.6).

Introduce a new basis with the states $|\tilde{1}\rangle$ and $|\tilde{2}\rangle$:

$$|\tilde{1}\rangle = h\left(c_2|1\rangle - |2\rangle\right),\tag{4.17}$$

$$|\tilde{2}\rangle = h(|1\rangle + c_2|2\rangle),$$
 (4.18)

$$h = \left(1 + c_2^2\right)^{-1/2} \tag{4.19}$$

instead of states $|1\rangle$ and $|2\rangle$; all other states coincide in the new and old bases. Obviously, the new basis is orthonormal. The non-diagonal elements of Hamiltonian matrix with the states $|\tilde{1}\rangle$ are all zero:

$$\langle \tilde{1}|H|j\rangle = 0 , \qquad j = \tilde{2}, 3, 4, \dots N ;$$
 (4.20)

in other words state vector $|\tilde{1}\rangle$ is orthogonal to all vectors $H|j\rangle$. This means that the state $|\tilde{1}\rangle$ is fully decoupled from all the other states. The diagonal elements of Hamiltonian matrix remain the same in new basis. In terms of S matrix this could be written as

$$\langle \tilde{1}|S|\tilde{1}\rangle = 1$$
, (4.21)

$$\langle \tilde{2}|S|\tilde{2}\rangle = \exp\left(-\pi \sum_{k\neq 1,2}^{N} \left|\langle \tilde{2}|H|k\rangle\right|^2 \frac{1}{|\beta - \beta_k|}\right) = \mathcal{D},$$
 (4.22)

where we define

$$\mathcal{D} \equiv \exp\left(-\pi \left(1 + c_2^2\right) \sum_{k \neq 1, 2}^{N} \frac{|V_{1k}|^2}{|\beta - \beta_k|}\right) . \tag{4.23}$$

Here we used the result (3.23) obtained above for the non-degenerate case. The desired S matrix element in the original basis is

$$\langle 1|S|1\rangle = h^2 c_2^2 \langle \tilde{1}|S|\tilde{1}\rangle + h^2 \langle \tilde{2}|S|\tilde{2}\rangle = h^2 (c_2^2 + \mathcal{D}). \tag{4.24}$$

This gives the state-to-state transition probability

$$P_{11} = h^4 (c_2^2 + \mathcal{D})^2 , (4.25)$$

which coincides with the earlier obtained result in (4.12).

D. Fully degenerate multistate model

Consider the case when two fully degenerated bunches of potential curves cross each other. The Hamiltonian of this model has form:

$$H = \begin{pmatrix} E_1 & 0 & \cdots & 0 & V & \cdots & V \\ \vdots & \ddots & \vdots & \vdots & & \vdots \\ 0 & 0 & \cdots & E_1 & V & \cdots & V \\ V & V & \cdots & V & E_2 & \cdots & 0 \\ \vdots & \vdots & & \vdots & \vdots & \ddots & \vdots \\ V & V & \cdots & V & 0 & \cdots & E_2 \end{pmatrix}$$
(4.26)

Let n be the number of potential curves with energy $E_1 = \beta_1 t$ and m be the number of potential curves with energy $E_2 = \beta_2 t$. The Hamiltonian matrix has dimension $(n + m) \times (n + m)$. Some transition probabilities for this model can be written down straight off as particular cases of formulas (4.15) and (4.16). The survival probabilities are

$$P_{jj} = \frac{1}{n^2} (p^{nm/2} + n - 1)^2 \qquad j = 1, \dots, n ,$$

$$P_{jj} = \frac{1}{m^2} (p^{nm/2} + m - 1)^2 \qquad j = n + 1, \dots, n + m .$$
(4.27)

The intraband transition probabilities are

$$P_{jk} = \frac{1}{n^2} (p^{nm/2} - 1)^2 \qquad j \neq k, \qquad j, k = 1, \dots, n ,$$

$$P_{jk} = \frac{1}{m^2} (p^{nm/2} - 1)^2 \qquad j \neq k, \qquad j, k = n + 1, \dots, n + m , \qquad (4.28)$$

where p is the standard Landau-Zener probability:

$$p = \exp\left(\frac{-2\pi|V|^2}{|\beta_1 - \beta_2|}\right). \tag{4.29}$$

The remaining (interband) probabilities one can obtain by using the normalization condition:

$$\sum_{j=1}^{n+m} P_{jk} = \sum_{k=1}^{n+m} P_{jk} = 1. (4.30)$$

From general considerations it can be concluded that all interband transition probabilities are equal, i.e.:

$$P_{jk} = P_{jk'}$$
, $j = 1, ..., n$, $k, k' = n + 1, ..., n + m$,
 $P_{jk} = P_{jk'}$, $j = n + 1, ..., n + m$, $k, k' = 1, ..., n$. (4.31)

Using (4.30) and (4.31) we obtain:

$$P_{jk} = P_{kj} = \frac{1}{nm} (1 - p^{nm}) , \qquad j = 1, \dots, n , \qquad k = n + 1, \dots, n + m .$$
 (4.32)

Thus in this highly degenerate multistate model there are only five different state-to-state transition probabilities defined by expressions (4.27), (4.28) and (4.32). This conclusion as well as quantitative results were tested by numerical calculations.

V. CONCLUSION

In this paper we consider calculation of state-to-state transition probabilities in the generalized multistate Landau-Zener model by summation of perturbation theory series. Due to specifics of generalized Landau-Zener Hamiltonian (linear growth with time), some of the integrals emerging in the perturbative expansions are singular and require special analysis. The singularities of these integrals are 'useful' in the sense that they effectively cancel other integrations, such that the analytical expressions are obtained for each term in the perturbative expansion. Subsequently, entire infinite series is summed with the result obtained in closed form. The technique of such calculations is one of the principal results of the present study.

The other group of results refers to the degenerate cases. In the general non-degenerate case we are able to evaluate only two transition probabilities: the survival probabilities

for diabatic potential curves with maximum and minimum slope. Such a situation when some state-to-state transition probabilities are expressed by simple analytical formulas, while others remain unknown is quite unconventional, although now we know another similar example: the multistate Coulomb model [22]. As long as the degeneracy conditions are introduced, the analytical expressions for some new state-to-state transition probabilities are obtained. For the case of extreme degeneracy, when two fully degenerate bands of diabatic potential curves cross each other, the full set of state-to-state transition probabilities was derived. Various degenerate cases are met in practice, for example, in the treatment of second order effects in Rydberg H atom in perpendicular electric and magnetic fields [21].

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^[1] L. D. Landau, Phys. Z. Sowjetunion 2, 46 (1932).

^[2] C. Zener, Proc. R. Soc. Lond. A 137, 696 (1932).

^[3] E. Majorana, Nuovo Cimento **9**, 43 (1932).

^[4] E. C. G. Stükelberg, Helvetica Physica Acta 5, 369 (1932).

^[5] Yu. N. Demkov and V. I. Osherov, Zh. Exp. Teor. Fiz. 53, 1589 (1967) [Sov. Phys. - JETP 26, 915 (1968)].

^[6] V. N. Ostrovsky and H. Nakamura, Phys. Rev. A 58, 4293 (1995).

^[7] Yu. N. Demkov and V. N. Ostrovsky, Phys. Rev. A 61, 032705 (2000).

^[8] Yu. N. Demkov and V. N. Ostrovsky, J. Phys. B **34**, 2419 (2001).

^[9] S. Brundobler and V. Elser, J. Phys. A **26**, 1211 (1993).

^[10] A. V. Shytov, Phys. Rev. A **70**, 052708 (2004).

^[11] M. V. Volkov and V. N. Ostrovsky, J. Phys. B 37, 4069 (2004).

^[12] B. E. Dobrescu and N. A. Sinitsyn. J. Phys. B **39**, 1253 (2006).

- [13] M. V. Volkov and V. N. Ostrovsky, J. Phys. B 39, 1661 (2006).
- [14] M. V. Volkov and V. N. Ostrovsky, J. Phys. B 38, 907 (2005)
- [15] Y. Kayanuma, J. Phys. Soc. Japan **53**, 108 (1984); **53**, 118 (1983).
- [16] Y. Kayanuma, Phys. Rev. Lett. 58, 2934 (1987).
- [17] Yu. N. Demkov and V. N. Ostrovsky, J. Phys. B 28 403 (1995)
- [18] Yu. N. Demkov, P. B. Kurasov and V. N. Ostrovsky, J. Phys. A 28 4361 (1995)
- [19] V. N. Ostrovsky and H. Nakamura, Phys. Rev. A **58** 4293 (1998)
- [20] T. Usuki Phys. Rev. B **56** 13360 (1997)
- [21] V. N. Ostrovsky, J. Phys. B 38, 1483 (2005).
- [22] V. N. Ostrovsky, Phys. Rev. A 68, 012710 (1-7) (2003).